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Research Article

Study on the Rheological Property of Cassava Starch Adhesives

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Abstract: The main goal of this study was to use cassava starch in the production of environmentally sound adhesives. 'Three-formaldehyde glue' pollutes the environment and harms to human health strongly, which widely used for wood-based panels preparation. Environment-friendly cassava starch adhesives were prepared using method of oxidation-gelatinization, insteading of the three formaldehyde glue. The effects of the quality ratio of starch and water, temperature and shear rate on the apparent viscosity of the adhesive were studied. The rheological eigenvalue of apparent viscosity was studied through nonlinear regression. The results showed that the apparent viscosity of cassava starch adhesives decreased with the increasing of temperature; the apparent viscosity decreased slowly with the increasing of rotor speed; the phenomenon of shear thinning appeared within cassava starch adhesives which was pseudo-plastic fluids. Cassava starch adhesives with characteristics of non-toxic, no smell and pollution could be applied in interior and upscale packaging.

Keywords: Apparent viscosity, cassava starch adhesives, rheological eigenvalue

INTRODUCTION

Currently, the resin system used in wood-based panel preparation was the three-formaldehyde glue, which mainly consists of Urea-Formaldehyde resin adhesive (UF), Phenolic resin adhesive (PF) and Melamine-Formaldehyde resin adhesive (MF), however, there was a fatal drawback of this type of resin adhesives, such as the release of free formaldehyde which not only polluted the environment but also harmed to humans strongly (Wu *et al*., 2009; Li *et al*., 2008; Zhang and Zhang, 2008). Starch had advantages of resource-rich, low-cost, versatile, non-toxic, no smell, pollution etc. What's more, the starch adhesive with well adhesion and film-forming properties was a class of natural adhesives (Ding, 2008; Chen *et al*., 2007, 2006).

As a renewable natural polymer materials, the starch which not only has active functional groups, as well as the outstanding characteristics to adapt to the requirements of environmental protection, but also with the advantages of resource-rich, low-cost, non-toxic and biodegradable is payed more and more attention in the field of adhesives. However, as an adhesive, the pure starch has a lot of inadequacies, such as water resistance, fluidity, permeability, storage stability and mechanical properties (Guo and Guo, 2007; Fu and Lu, 2008; Syed *et al*., 2001; Liu *et al*., 2008; Santayanon and Wootthikanokkhan, 2003; Shi *et al*., 2008), the properties of starch could be improved by physical and chemical methods, for example, it was an effective way to change the solubility, viscosity and related properties to meet the performance requirements of different application areas. In both methods, the chemical modification was an important means of preparation of starch adhesives (Liu *et al*., 1999; Shi and Wang, 2006; Lin *et al*., 2007). The starch molecules contained the glycosidic bond and reactive hydroxyl groups could chemically react with many substances, which was the basis of chemically modified starch (Li *et al*., 2007).

In this study, we reported an easy method to prepare cassava starch adhesives through oxidation-gelatinization, insteading of the three formaldehyde glue. The aim of this study is to improve the apparent viscosity of cassava starch adhesives. Also, the effects of the quality ratio of starch and water, temperature and shear rate on the apparent viscosity of the adhesive were studied. The rheological eigenvalue of apparent viscosity was studied through nonlinear regression.

MATERIALS AND METHODS

The raw materials, reagents and their grades and manufacturers, are listed in Table 1.

Methods: There are many methods to prepare cassava starch adhesives and in this test, the method of oxidation-gelatinization was used to prepare cassava

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Table 1: The raw materials of experiments

The main raw material	Trademark	Manufacturer
Cassava starch	Edible starch	Shandong Jincheng Food Co., Ltd.
30% H_2O_2	AR	Nanjing Chemical Reagent Co., Ltd.
NaOH solution	AR	Nanjing Chemical Reagent Co., Ltd.
$Na_2S_2O_3$	AR	Nanjing Chemical Reagent Co., Ltd.
$FeSO_4{\cdot}7H_2O$	AR	Nanjing Chemical Reagent Co., Ltd.

Table 2: Formula of preparing cassava starch adhesives

The appellation	H_2O_2	Fe^{2+} solution	NaOH solution	$Na_2S_2O_3$ solution
Concentration	26%	6%	10%	6%
Dosage	0.5 mL	1 mL	18 mL	2 mL
Effect	Oxidizer	Oxidizer	Pasting agent	Blockers

starch adhesives. Table 2 is the formula of preparing starch adhesives.

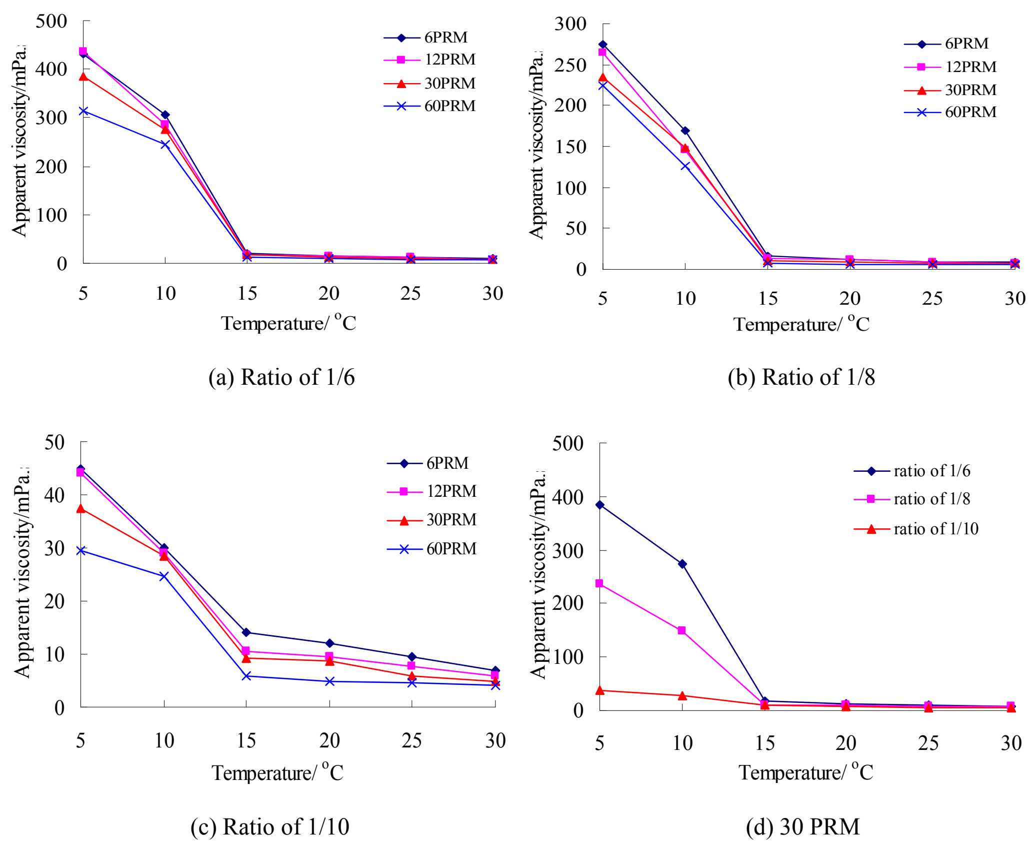
Analysis methods: In accordance with the national standard GB/T 2794-1995 "the adhesive viscosity measurement", the NDJ-5S digital viscometer was used to test the starch adhesive viscosity. Before measuring, the viscosity of the liquid to be measured should be estimated firstly and then the suitable rotor and rotational speed of the digital viscometer were selected. To ensure the accuracy, the percentage of the range should be accurately controlled in the range of 10 to 90% and the sample of starch adhesives should be uniformly and without bubbles during the measurement. The samples were measured after half an hour of the temperature converted and the temperature should been reached the set value each time.

Starch adhesives put into the beaker which placed in the bath pot with a constant temperature while measuring the viscosity of starch adhesives. The rotor immersed into the adhesive in depth properly and then selected the appropriate speed by the control panel keys. The average of five measurements of the apparent viscosity of the starch adhesive was considered to be the result.

RESULTS AND DISCUSSION

Adhesive viscosity has an important role on the bonding strength, tensile strength and other mechanical properties in the composite materials. The starch adhesives apparent viscosity depends on the dispersion of the starch molecules in solution expand capacity, where the starch molecules increase the content area and reinforce mutually during the adhesive preparation process and ultimately enhance the adhesion strength.

Figure 1 shows the effect of temperature on apparent viscosity of cassava starch adhesives. As can be seen from the figure, when the ratio of starch and water quality was 1/6, cassava starch adhesives



(a) Ratio of 1/6 (b) Ratio of 1/8

(c) Ratio of 1/10 (d) 30 PRM

Fig. 1: Effect of temperature on apparent viscosity of cassava starch adhesives

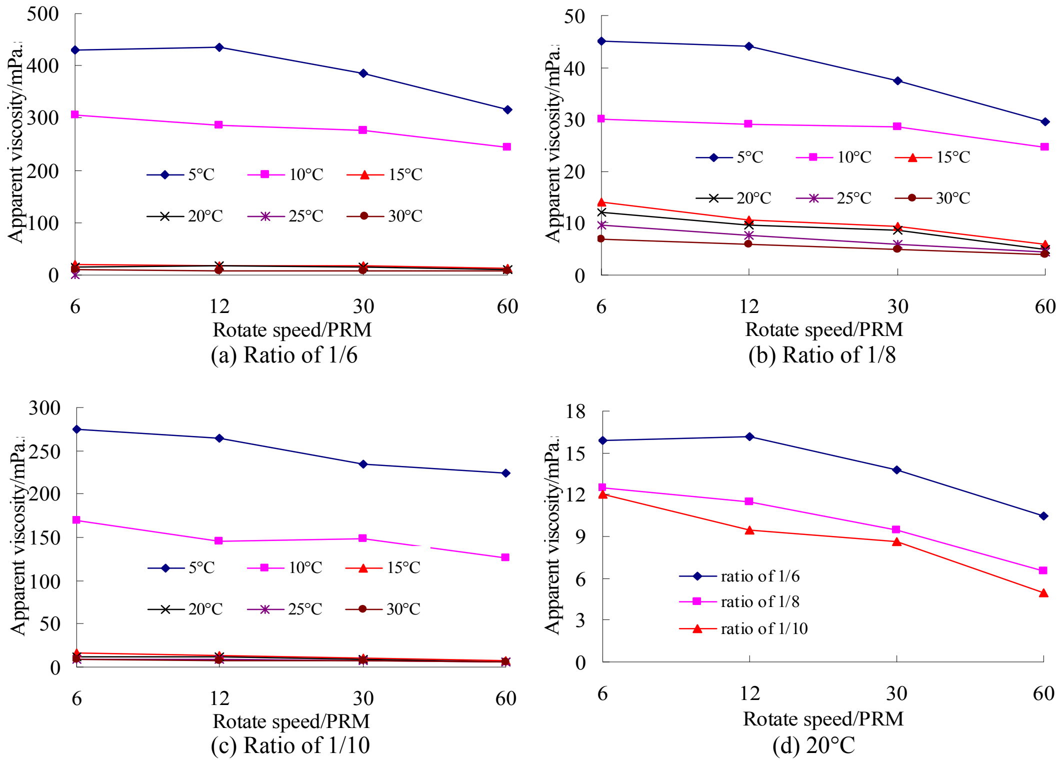


Fig. 2: Effect of rotate speed on apparent viscosity of cassava starch adhesives

apparent viscosity decreased with the increase of the temperature. The corresponding maximum value was 430, 435, 385 and 315 mPa.s, respectively, but the descending of apparent viscosity was quick within 15°C, the decline of the rate of the apparent viscosity decreased gradually after 15°C (Fig. 1a). When the ratio of starch and water was 1/8, the maximum value of apparent viscosity (275, 265, 235 and 225 mPa.s when speed was 6, 12, 30 and 60 PRM, respectively) was obtained at 5°C and the descending of apparent viscosity was quick within 15°C also, then the descending was slow (Fig. 1b). While the ratio of starch and water was 1/10, the peak of the apparent viscosity (45, 44, 37.5 and 29.5 mPa.s when speed was 6, 12, 30 and 60 PRM, respectively) was obtained at 5°C and the apparent viscosity decreased gradually with the increase of the temperature (Fig. 1c). While the ratio was 1/6, the adhesive prepared apparent viscosity was significantly better than the other two adhesive. As is portrayed in Fig. 1d, when the speed was 30 PRM, the peak values (385, 235 and 37.5 mPa.s when the ratio of starch and water was 1/6, 1/8 and 1/10, respectively) were obtained, the apparent viscosity decreased with the increase of the temperature, what's more, the higher the temperature was, the smaller the difference between the apparent viscosity of the different adhesives, this may be due to the raise in temperature make the frictional resistance among starch molecules smaller, which manifested as the decrease of the viscosity.

Figure 2 shows the effect of rotate speed on apparent viscosity of cassava starch adhesives. As can be seen from the figure, the apparent viscosity decreased slowly with the increase of the speed of the rotor, that's can be explained that the phenomenon of shear thinning appears in cassava starch adhesives, when the ratio of starch and water was 1/6, the apparent viscosity of adhesives was significantly better than the other two adhesives that was prepared with 1/8 and 1/10 of ratio of starch and water, the peak values (15.9, 12.5 and 12 mPa.s, respectively) were obtained at 20°C.

As can be seen from Fig. 1 and 2, with many strongly hydrophilic functional hydroxyl groups in the main chain of the starch molecules, the hydroxyl groups bonded to each other to form hydrogen bonds, so that the starch adhesive would have a certain adhesion force, however, the cohesion of the hydroxyl group with water molecules is much larger than the binding force among the starch molecules, the absorption of hydroxy on glued materials was desorbed by water molecules, as a result, the wet bonding strength of the starch adhesive degraded severely and the effect of temperature on adhesives was greater than the two precious.

The value of k, n and the correlation coefficient R^2 of adhesives were obtained by using one unknown nonlinear regression to analyze the apparent viscosity and shear rate. Table 3 to 5 show the rheological eigenvalue of cassava starch adhesives apparent viscosity with the ratio of 1/6, 1/8 and 1/10, respectively.

As is depicted in Table 3 to 5 cassava starch adhesives prepared in this test were pseudo-plastic

Table 3: Rheological eigenvalue of cassava starch adhesives (ratio of 1/6)

Temperature/°C	$k/Pa.s^n$	n	Expression	R^2
5	577.230	-0.1349	$\eta = 577.23v^{-0.1349}$	0.8323
10	357.840	-0.0875	$\eta = 357.84v^{-0.0875}$	0.9321
15	28.381	-0.1703	$\eta = 28.381v^{-0.1703}$	0.9044
20	23.573	-0.1795	$\eta = 23.573v^{-0.1795}$	0.8227
25	16.445	-0.1416	$\eta = 16.445v^{-0.1416}$	0.7380
30	12.058	-0.1366	$\eta = 12.058v^{-0.1366}$	0.9973

Table 4: Rheological eigenvalue of cassava starch adhesives (ratio of 1/8)

Temperature/°C	$k/Pa.s^n$	n	Expression	R^2
5	327.740	-0.0932	$\eta = 327.74v^{-0.0932}$	0.8289
10	200.340	-0.1070	$\eta = 200.34v^{-0.107}$	0.8118
15	30.455	-0.3363	$\eta = 30.455v^{-0.3363}$	0.9538
20	21.720	-0.2737	$\eta = 21.72v^{-0.2737}$	0.9056
25	13.995	-0.1899	$\eta = 13.995v^{-0.1899}$	0.8774
30	12.262	-0.1831	$\eta = 12.262v^{-0.1831}$	0.9210

Table 5: Rheological eigenvalue of cassava starch adhesives (ratio of 1/10)

Temperature/°C	$k/Pa.s^n$	n	Expression	R^2
5	65.761	-0.1822	$\eta = 65.761v^{-0.1822}$	0.8958
10	35.054	-0.0770	$\eta = 35.054v^{-0.077}$	0.7899
15	26.079	-0.3427	$\eta = 26.079v^{-0.3427}$	0.9258
20	22.967	-0.3431	$\eta = 22.967v^{-0.3431}$	0.8773
25	16.812	-0.3154	$\eta = 16.812v^{-0.3154}$	0.9914
30	10.815	-0.2370	$\eta = 10.815v^{-0.237}$	0.9891

fluids because all of the n were less than zero. When the rheological curve of cassava starch adhesives was described by the pseudo-plastic fluid model, the model could better describe the rheological properties of cassava starch adhesives curve if R^2 was between 0.5776 and 0.9914.

CONCLUSION

- Cassava starch adhesives apparent viscosity decreased with the increase of the temperature.
- The apparent viscosity decreases slowly with the increase of the rotor speed and the phenomenon of shear thinning appears in cassava starch adhesives.
- Cassava starch adhesives are pseudo-plastic fluids.

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